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PATENT SPECIFICATION 1,190,682

DRAWINGS ATTACHED.

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COMPLETE SPECIFICATION.

Concentration of Aqueous Formaldehyde Solutions.

We, SOCIETA' ITALIANE RESINE S.p.A., an Italian Joint Stock Company, of 33, Via Grazioli, Milan, Italy, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for obtaining concentrated aqueous formaldehyde solutions from aqueous solutions of lower concentrations.

For concentrating aqueous formaldehyde solutions two distilling techniques have been developed which operate either under vacuum or at atmospheric or superatmospheric pressures. Since in the latter case compositions of sufficiently high concentration cannot be obtained, the operation is mostly carried out at low pressure and hence at low temperature, to obtain high formaldehyde concentrations.

However, it is known that at each concentration of the solution there is a temperature, called the "stability temperature", below which solid polyoxymethylenes precipitate. An aqueous solution of formaldehyde is stable at relatively elevated temperatures, but on lowering the temperature a point is reached at which the formaldehyde polymerises and solid polyoxymethylene particles start precipitating. This stability temperature depends on the concentration of the formaldehyde in the solution, and thus the temperatures and hence the pressures at which the distilling process can be carried out are limited.

When distilling under vacuum, special measures are therefore taken, such as creating a high drop in pressure between the individual trays of one or more distilling columns, with a view to maintaining the temperature of the base products, which are of high formaldehyde concentration, at a value exceeding that at which the mass solidifies. However, this entails considerable constructional complications. Moreover, owing to the long contact times distinguishing these processes, apparatus of considerable size is required, which is economically undesirable. Finally, a further disadvantage deriving from the long contact time of the formaldehyde solutions at high temperatures, which may even be higher than the temperatures at which polymer precipitates, consists in the formation of side products such as methanol and formic acid (the Cannizzaro reaction) as well as in the formation of sugars.

It has now been found according to the invention that aqueous formaldehyde solutions can be concentrated by operating under vacuum levels the same as or even lower than vacuum levels adopted heretofore, without, however, the necessity of raising the temperature of the base solution above its stability limit.

The invention is based on the discovery that below the stability temperature a specific time elapses before the concentrated aqueous solution solidifies or gives rise to the precipitation of solid bodies.

A given period of time is therefore available, which is a function of the formaldehyde concentration and temperature, for handling the solution in liquid state without solidification risk. It has been found that this time shortens as the formaldehyde concentration increases and as the difference between the operating temperature and stability temperature of the aqueous formaldehyde increases.

Moreover, this period of time is affected by impurities in the product, such as formic acid or methanol.

Though stabilizing compounds may be added to the process of the present invention which are capable of delaying or avoid-

ing precipitation in formaldehyde solutions, these additions are neither desirable nor necessary for the purposes of the process, since they would increase costs and decrease the purity of the final product.

Accordingly, the present invention is a process for concentrating aqueous formaldehyde solutions by distillation, wherein the concentration is effected under reduced pressure in one or more distillation steps, the distilaltion temperature of each stage being below the stability temperature of the concentrated aqueous solution formed therein and said concentrated solution being subjected to said distillation temperature for a period shorter than that required for the solution to become turbid or for solid bodies to appear therein, and wherein the concentrated aqueous solution of each stage, after formation, is subjected to an ageing period at a temperature exceeding the stability temperature of said concentrated solution.

Any suitable apparatus may be used for distillation, especially apparatus for so-called 'instantaneous" distillation, such as thin film evaporators or molecular distillation apparatus.

When concentrating commercial formaldehyde (30—36% solutions) the operation can be carried out in one stage but, considering the losses of formaldehyde in the head vapours, two or more consecutive steps are preferably employed, each of which is carried out under vacuum at a temperature below the stability temperature of the concentrate produced in that stage, an ageing period for the formaldehyde solution being concentrated being interposed between the individual steps, at a temperature exceeding the stability temperature. In this manner a formaldehyde solution is obtained as a final product, which titrates over 75—85%, and formaldehyde losses are substantially avoided.

Thus, the formaldehyde concentration process of the present invention, starting from aqueous formaldehyde, is simple and economically convenient and yields a pure clear product which is useful as a source of formaldehyde and is suitable for conversion, for instance to the mixture of formaldehyde polymers known by the name of paraformaldehyde.

When concentrating commercial 30—36% formaldehyde solutions, the preferred embodiment of the invention comprises a first instantaneous evaporation leading to compositions titrating approximately between 55 and 65% formaldehyde, followed by an ageing period, the aged product then being evaporated in a second instantaneous evaporation to yield a composition titrating over 75%, preferably between approximately 80 and 86% formaldehyde.

Finally, after a further ageing period above the stabflity temperature, the clear liquid formaldehyde produced may be used as such or converted for instance to paraformaldehyde by the conventional polymerization processes in the absence or in the presence of catalysts.

Still in accordance with the preferred embodiment, the head products obtained by the second instantaneous evaporation are recycled to the first evaporator.

The head products of the first evaporation having a very low formaldehyde titre may be recycled to the washing towers in the manufacture of commercial formaldehyde, thereby replacing in part the washing down water. By using this procedure the formaldehyde losses are practically nil.

Three or more consecutive concentration stages by evaporation may also be adopted in order to obtain either a product titrating over 87% (up to about 95%) or a head product at the first evaporator having a practically nil (below 0.5%) formaldehyde concentration, such that it can be discarded.

Thus the expert may easily find a course by which formaldehyde losses are practically nil and the formaldehyde concentration in the discharge waters is such as not to disturb normal operation of the purifying plants.

During each evaporation step the temperature is preferably maintained below 100°C, more particularly 5° or more below the stability temperature of the composition at the base, of the column, such temperatures in degrees centigrade being numerically approximately equal to the concentrations in percent by weight of formaldehyde.

During the ageing period the temperature is preferably maintained at a value of at least 5°C, preferably 10° to 30°C, above the stability temperature, for a period of 0.5 to 30 minutes, preferably 2 to 20 minutes.

The invention is further illustrated by the following Example which, however, should not be understood as a limitation of the scope of the invention.

EXAMPLE

Commercial formaldehyde titrating to an equivalent of 36% by weight formaldehdye is continuously concentrated by means of three thin film evaporators A, B, and C arranged in series as shown in the accompanying drawing in which the single figure is a schematic view of the three evaporators. The thin film evaporators are formed by a double jacketed vertical tube for steam heating, and a stellate shaped stirrer (not shown) distributes the liquid fed at the top of each evaporator by centrifugal effect, in the form of a thin layer on the walls of the heating tube.

The vapours issue at the top of the tubular evaporators, and the concentrate is removed at the base by a pump (not shown), and then passed to a heat-exchanger and heated to ageing temperature at a rate such that the residence time of the liquid from its inlet to the evaporator to its removal from the heat exchanger is 2 minutes.

After removal from the heat exchanger, the concentrate is maintained for 7 minutes in the ageing apparatus (M).

70 parts by weight/hour commercial formaldehyde are conveyed to evaporator B through 1, together with the base product of the evaporator (A) and the head product of the evaporator (C).

The evaporating and aging temperatures in the evaporators (A), (B) and (C) in degrees centigrade are 18, 40; 43, 70; and 62, 102, respectively.

29.5 parts by weight per hour of colorless clear concentrated formaldehyde are obtained, titrating 84% formaldehyde by weight, which is discharged through 2.

The condensate from the evaporator (A) titrates 0.45% formaldehyde and is discharged through 3.

It will be obvious to those skilled in the art that a very simple highly economical process can be carried out by exploiting the principles of the heat recovery; for instance, it is possible to decrease considerably the amount of heat required for evaporation if the vapours from the evaporator (C) are used for heating the evaporator (B), and the vapours from the evaporator (B) are used for heating the evaporator (A). Moreover, the apparatus according to the example is suitable for concentrating formaldehyde solutions of any concentration ranging between about 1 and 70% by weight which may be conveyed, depending upon their formaldehyde content, to the evaporator (A), (B) or (C).

WHAT WE CLAIM IS:—

1. A process for concentrating aqueous formaldehyde solutions by distillation, wherein the concentration is effected under reduced pressure in one or more distillation steps, the distillation temperature of each stage being below the stability temperature as defined hereinbefore of the concentrated aqueous solution formed therein and the said concentrated solution being subjected to said distillation temperature for a period shorter than that required for the solution to become turbid or for solid bodies to appear therein, and wherein the concentrated aqueous solution of each stage, after formation, is subjected to an ageing period at a temperature exceeding the stability temperature of said concentrated solution.

2. Process as claimed in claim 1, characterized in that the temperature is maintained during each evaporating step at a value below 100°C, the preferred temperatures being lower by 5°C than the stability temperature of the concentrated solution produced in each evaporation step.

3. Process as claimed in Claim 1 or 2, characterized in that the ageing temperatures of the formaldehyde compositions exceed by at least 5°C; preferably by 10 to 30°C, the stability temperatures.

4. Process as claimed in Claim 2 or 3, characterized in that the ageing period following each evaporating step ranges between 0.5 and 30 minutes, preferably between 2 and 20 minutes.

5. Process as claimed in any of the preceding claims, characterized in that evaporation of the aqueous formaldehyde solution is carried out by the thin film layer technique.

6. Process substantially as hereinbefore described with reference to the example.

7. Concentrated aqueous formaldehyde solutions, whenever preferred by a process according to any of the preceding claims.

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1 SHEET *This drawing is a reproduction of the Original on a reduced scale*